The Swedish Club

CARGO ADVICE

Hazardous chemical cargoes

Introduction

A large range of chemical commodities are carried on board chemical tankers, totalling more than 5,000 different chemical products and grades. These chemical products often have a high minimum purity due to their intended end uses.

The contamination of chemical cargoes can often affect the suitability for their intended end use, and this can play a significant role in the cargo's value. As a result, special consideration should be given towards these sensitive cargoes in order to ensure their proper carriage.

Guidelines for the shipment of hazardous chemical cargoes

1. Pre-loading

The large variety of different chemical cargoes carried by chemical tankers means that there is a possibility of incompatible products being carried consecutively. As a result, special attention must be paid to ensuring cargo tanks are thoroughly cleaned. Very large industry standard cleaning matrices are available covering the various grade changeover combinations.

In order to ensure sufficient tank preparation has been carried out, thorough pre-loading surveys of a vessel's cargo tank/pump/heating equipment/ lines will be performed, including visual inspection of tanks together with wall-wash tests, when appropriate, prior to the loading of a 'first foot' trial quantity of cargo.

In addition to the pre-loading surveys often carried out by shippers' surveyors, first foot sampling methods can give a good indication of the cleanliness of cargo tanks and lines. This is because any contaminants present in the shore or vessel lines or the cargo tanks will be concentrated in the first foot samples.

However, tanks coated with epoxy type coating systems can absorb light solvent species, such as aromatics, which may not immediately be detected during pre-loading inspections.

As with residues of previous cargoes, water is undesirable in high purity chemical cargoes. Moisture can enter a cargo via insufficient tank/line ventilation and draining of wash water, although this will typically be detected in the pre-loading survey and first foot samples.

Are the vessel's tanks suitable to carry the nominated cargo?

- What are the previous three cargoes carried by the vessel?
- Is the cleaning from the previous cargo in line with industrial guidelines, such as *Dr Verwey's* or *Miracle*?
- Are cargo tanks and cargo lines dry?
- Do the cargo tanks need to have a nitrogen blanket or a specific oxygen content?

2. During loading, voyage and discharge

Mono ethylene glycol (MEG)

MEG is a precursor used in the manufacture of polyester and polyethylene terephthalate (PET) resins. MEG is shipped as a high purity compound; the quality parameters critical for the shipment of MEG are as follows:

- **Water:** MEG is hygroscopic. Water absorption can be reduced by ensuring tanks and lines are well drained and by applying a nitrogen blanket to the cargo immediately upon completion of loading.
- **Ultra-violet transmission (UVT):** The UVT parameter is used to indicate the presence of trace levels of aromatic hydrocarbon species (benzene, toluene, xylene etc). These species are detrimental to the ability to process MEG to form polyesters. Tank cleaning should be performed thoroughly, and consideration made as to cargo sequencing to avoid leeching from epoxy coatings – it takes only several ppm of aromatics to bring MEG off-specification for UVT, and product which contains aromatics, such as pyrolysis gasoline can also affect this parameter.
- **Chlorides:** Chlorides are undesirable for the onward processing of MEG parcels. Proper tank cleaning and rinsing with fresh water following any seawater washes can help to remove chloride containing residues.

Styrene Monomer (SM)

SM falls under a group of cargoes known as 'inhibited monomeric cargoes', which also includes isoprene monomer.

Monomeric cargoes can be highly reactive and undergo a self-propagating polymerisation process until all of the desirable cargo is depleted. This not only leads to a loss in useable cargo but can be hazardous due to the formation of heat during the reaction. Extensive polymerisation also forms solidified products which are extremely difficult to remove from the cargo tanks. Several factors should be considered for carriage of a monomer cargo:

- **Inhibitor concentration:** Such polymerisation processes can be prevented by the presence of an inhibitor, which in the case of styrene monomer is 4-tert-Butylcatechol (TBC). Guidelines are available regarding the concentration of inhibitor required for a given cargo temperature and storage time.
- **Cargo temperature control:** Ensuring temperatures are kept to a minimum reduces the rate of inhibitor depletion and polymerisation. For cargoes of butadiene, formation of a dimer (the product when two monomers join) is inevitable but can be minimised by ensuring the product is carried at the coolest practicable temperature.
- **Dissolved oxygen content:** The mechanism by which TBC inhibits the styrene monomer reacting relies on the presence of dissolved oxygen in the cargo. Cargoes should be loaded onto the vessel with sufficient dissolved oxygen for effective inhibition, while the tank atmosphere should be made inert to minimise explosion risk, but contain sufficient oxygen to maintain dissolved oxygen levels. Charterers'/shippers' instructions to maintain oxygen content of the 'inert' headspace should be followed, and tank atmosphere oxygen levels monitored routinely.

Phenol

Phenol is used primarily as a feedstock in the production of precursors to plastics and epoxy resins, particularly via reaction with acetone in the production of bisphenol A. Phenol is also used in the production of fine chemicals such as pharmaceuticals, where a very high purity is required.

Phenol has a propensity to discolour from being colourless to becoming a yellow or pink colour if exposed to high heat, air and/or sunlight. The following factors should be considered when stowing phenol to prevent discolouration and other quality issues:

- **Exclusion of air:** Carriage and replenishment of nitrogen overpressure is recommended during carriage and following part-discharge operations. This reduces the rate of discolouration and moisture ingress – phenol is hygroscopic and so absorbs moisture from the air during storage.
- **Stowage temperature:** With a melting point of approximately 41°C, phenol requires heating during the voyage, preferably through use of steam heating coils in the tanks. However, care should be taken to avoid overheating the cargo and detailed heating and tank atmosphere (pressure/O_2 content) records should be retained.
- **Removal of sunlight:** Samples should be carefully stored in cool, dark places out of direct sunlight to

avoid deterioration of colour. Sampling in amber glass bottles assists in preventing deterioration, but with the drawback of making rapid colour observations difficult.

Methanol

Methanol is the largest volume chemical commodity shipped worldwide and is used principally in the manufacture of formaldehyde resins but has a large number of other industrial uses. As with MEG, methanol is sensitive to chloride, aromatics and moisture content.

Proper tank cleaning should be performed, and consideration should be given towards the stowage plan and previous cargoes carried by the vessel. An increasing amount of methanol trade is performed using dedicated tankers, eliminating cross-contamination concerns.

Acetone

Acetone is a commercially important commodity used as a solvent and in the production of nylon and polycarbonate resins.

As with methanol, acetone is a good solvent and very sensitive to impurities including moisture and chloride.

The permanganate fade time (PFT) test, indicative of the presence of oxidisable contaminant species, is also a critical quality parameter, and can be affected by traces of impurities or formation of species by inherent instability. Acetone should not be held adjacent to cargoes heated to above 35°C to preserve storage life. As a strong solvent, acetone can soften epoxy coated tanks and easily remove absorbed aromatics, therefore, use of stainless-steel tanks is advisable.

n-butanol

n-butanol is a colourless, sweet liquid shipped as a high purity cargo. The largest use for n-butanol is in the production of varnishes and as a chemical precursor, such as in the manufacture of butyl acetate which is an artificial flavouring and solvent.

As with other water-miscible chemical cargoes such as methanol and acetone, water content is a sensitive quality parameter along with purity. Therefore, cargo tanks should be cleaned and dried thoroughly before loading, but wall wash tests are not typically required. The flash point of n-butanol is approximately 34°C, meaning that it should be transported at ambient temperature and not stowed adjacent to any heated cargoes. The application of a nitrogen blanket may not be required for safe transportation depending on the age of the vessel and the tank size, although may be requested by the charterers to reduce moisture ingress.

3. Risks associated with carriage

Unstable cargoes

Many cargoes carried on board chemical tankers are prone to undergoing chemical reactions, either by themselves (i.e. self-polymerisation) or with impurities or air. These reactions reduce the purity of the products and in some cases can generate large amounts of heat which presents a safety risk.

Depending on the exact cargo involved, there are several factors which must be considered when stowing cargoes with a limited 'shelf-life', such as:

- Oxygen content
- Inhibitor content
- Temperature

Temperature

High temperatures generally increase the rate of chemical reactions – an increase in 10°C is often said to double the rate of many chemical processes, and therefore increased storage temperatures lead to a reduced 'shelf-life' of the chemical.

Nevertheless, some cargoes require heating to ensure fluidity during cargo operations to prevent short delivery. In order to prevent overheating, strict control of temperatures is required to ensure a balance between fluidity and chemical stability in order to prevent both shortage and quality disputes.

Other products, such as isoprene, are sensitive to heat to the extent that they require cooling to maintain low temperature.

For these reasons, it is important for a vessel's crew to refer to voyage heating instructions and ensure cargo temperatures are monitored at least once or twice daily, at upper, middle and lower levels through the cargo column, to ensure cargo temperatures are within the recommended range.

Sensitivity to air

Some chemical cargoes are particularly reactive towards oxygen and, as such, control of tank atmosphere may also be required by way of nitrogen blanketing for partial or total exclusion of oxygen (for example with propylene oxide/hexamethylene diamine-HMD).

Partial reduction of oxygen is also warranted for a range for oxygen dependent inhibited cargoes, such as styrene and isoprene monomers, to prevent self-polymerisation.

The exclusion of air, or specifically the oxygen in air, is also commonplace when carrying flammable cargoes (flash point <60 °C). Recent changes to the IBC code (International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk) in 2021 has meant that inerting of low flash point cargoes may now be mandatory depending on the age of the vessel and the tank size, and therefore the IBC code should be consulted prior to carrying low flash point cargoes.

Moisture

Some cargoes may be required to be carried under nitrogen as they are susceptible to absorbing moisture from the air. This reduces the exposure of the cargo to moisture in air during transport. Examples of hygroscopic cargoes (cargoes which absorb moisture easily) are MEG, phenol and methanol.

Conclusion

Most voyages with hazardous chemical cargoes will be uneventful, but sometimes things go wrong. To minimise the risk of a claim of contamination resulting from the mishandling of the cargo, it is important that correct measures as described above are taken during loading, voyage and discharge.

Loss prevention essentials

- Ensure that the stowage plan is suitable. When stowing cargo in adjacent tanks pay attention to cargo carriage temperature restrictions. This is especially important when the vessel is loading cargo at several ports.
- Comply with charterers' carriage instructions, paying particular attention to temperature and oxygen content. If these are unclear, seek clarification.
- Monitor the temperature of the cargo at upper, middle and lower levels through the cargo column at least once a day during the voyage to ensure compliance with heating rates and carriage temperatures, where appropriate.
- Recirculate the cargo if required. This is important for inhibited cargoes which depend on dissolved oxygen content to maintain inhibition.